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1746

| TRANSMITTAL LETTER | | | Case No. 11038/3 |
|---|------------------------------------|-------------------------------|-------------------------------|
| Serial No. 09/831,931 | Filing Date May 15, 2001 | Examiner J. Crepeau | Group Art Unit 1746 |
| Inventors SOREN PRIMDAHL, CARSTEN BAGGER, METTE JUHL JORGENSEN, MOGENS MOGENSEN and OLGA MARINA | | | |
| Title of Invention ELECTROCHEMICAL CELL | | | |

TO THE COMMISSIONER FOR PATENTS

Transmitted herewith is a Supplement To Response Under 37 C.F.R. § 1.111; Declaration Of Mogens Mogensen
under 37 C.F.R. § 1.132 (with attached Exhibit A); and

- ☐ Small entity status of this application under 37 CFR § 1.27 has been established by verified statement previously submitted.
- ☐ A verified statement to establish small entity status under 37 CFR §§ 1.9 and 1.27 is enclosed.
- ☐ Petition for a _____ month extension of time.
- ☒ No additional fee is required.
- ☐ The fee has been calculated as shown below:

| | Claims Remaining After Amendment | | Highest No. Previously Paid For | Present Extra |
|---|---|-------|---------------------------------------|------------------|
| Total | | Minus | | |
| Indep. | | Minus | | |
| First Presentation of Multiple Dep. Claim | | | | |

| Small Entity | | or | Other Than Small Entity | |
|--------------------|--------------|----|----------------------------|--------------|
| Rate | Add'l Fee | | Rate | Add'l Fee |
| x \$9 = | | | x \$18 = | |
| x 42 = | | | x \$84 = | |
| + \$140 = | | | + \$280 = | |
| Total add'l fee | \$ | | Total add'l fee | \$ |

- ☐ Please charge Deposit Account No. 23-1925 (BRINKS HOFER GILSON & LIONE) in the amount of \$_____.
A duplicate copy of this sheet is enclosed.
- ☐ A check in the amount of \$_____ to cover the filing fee is enclosed.
- ☒ The Commissioner is hereby authorized to charge payment of any additional filing fees required under 37 CFR § 1.16 and any patent application processing fees under 37 CFR § 1.17 associated with this communication or credit any overpayment to Deposit Account No. 23-1925. A duplicate copy of this sheet is enclosed.
- ☒ I hereby petition under 37 CFR § 1.136(a) for any extension of time required to ensure that this paper is timely filed. Please charge any associated fees which have not otherwise been paid to Deposit Account No. 23-1925. A duplicate copy of this sheet is enclosed.

Respectfully submitted,

Jasper W. Dockrey
Jasper W. Dockrey, Registration No. 33,868
Attorney for Applicants
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I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail, with sufficient postage, in an envelope addressed to: Mail Stop Non-Fee Amendment, Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450, on March 17, 2004.

Date: March 17, 2004Signature: *Jasper W. Dockrey*

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Name of applicant, assignee or
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Signature

March 17, 2004

Date of Signature

Case No.: 11038/3

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

PRIMDAHL et al.

Serial No.: 09/831,931

Filing Date: May 15, 2001

For: ELECTROCHEMICAL CELL

Examiner:

J. Crepeau

Group Art Unit:
1746

**DECLARATION OF MOGENS MOGENSEN
UNDER 37 C.F.R. § 1.132**

I, Mogens Mogensen am a co-inventor of the above-referenced patent application and I hereby declare as follows:

1. I hold a Ph. D. degree from The Technical University of Denmark. I am presently employed in the Materials Research Department , Risoe National Laboratory, Denmark and hold the position of Research Professor in SOFC. I have worked in the area of solid oxide fuel cell ("SOFC") technology for 16 years. In association with my research and engineering activity, I have published 170 articles and I hold 5 patents in the area of SOFC technology.

2. I have reviewed the instant Office Action dated September 2, 2003, and the earlier Office Action dated February 26, 2003. I have also reviewed the English abstract and English machine translation of the prior art reference JP 5,190,183, and U.S. Pat. No. 5,908,713. It is my belief that these references do not suggest or disclose my invention as recited in the amended claims set forth in the Response filed herewith.

3. As set forth in my patent specification, an electrode having a relatively small concentration of Mn in a portion of the electrode extending less than about 20 microns from the electrolyte produces an SOFC having improved performance characteristics. In particular, in Table 1A in my specification, I show that Ni-based electrodes having a first layer containing 2.4% and 4.6% MnO₂ respectively have less polarization resistance R_p when compared with a reference electrode that does not contain MnO₂. (Specification, pg. 11). The structure of the inventive electrode is schematically depicted in FIGs. 1 and 2 of my drawing. As I describe at page 3, the electrode is electrochemically active in a range of about 10 to 20 microns from the sintered electrolyte. (Specification, pg. 3, ll. 24-25; pg. 4, ll.1-3). Accordingly, this layer is associated with the lowest achievable R_p . The data shows a significant reduction in R_p when the active electrode layer (18) includes 0.5 to 6 metal atom% Mn and has a thickness of less than about 20 microns.

4. In Table 1B of my specification I show experimental data illustrating a substantial improvement in the in-plane conductivity σ in Ni-based electrodes having 4.1% MnO₂ when compared with reference electrodes that do not contain MnO₂. (Specification, pg. 14). The electrode material containing the MnO₂ was applied as a thin layer to the electrolyte. (Specification, pg. 12, ll. 13-18). The active electrode layer (23) is schematically shown in FIG. 5 and has a thickness of less than about 20 microns.

5. The experimental results described above and fully set forth in my specification point to the improved fuel cell performance that is obtained when a relatively low Mn concentration is established in the electrochemically active region near the electrolyte. It is my belief that the performance improvement that I describe in my specification is not suggested or disclosed by JP 5,190,183, or U.S. Patent No. 5,908,713.

6. The unexpected results of my invention are demonstrated by experiments that I have performed which show that if the entire anode of an SOFC has a Mn concentration within the claimed range, the fuel cell will break down within a few days of commencing operation. I believe that migration of MnO_x to the electrode/electrolyte interface will react excessively at the YSZ grain boundaries and cause the electrode to delaminate from the electrolyte.

In Attachment A, I present my experimental data as reported in the document titled "Development of Thin-Electrolyte Solid Fuel Cells" by Dent Kammer, Peter Halvor Larsen, Ye-Lin Liu, Bruno Kindl and myself.

The results of my experiments show that the region within about 20 microns of the electrolyte is electrochemically active. The beneficial effects of my invention are realized if MnO_x is only added to the anode in a defined region within about 20 microns of the electrolyte. It is my belief that the mechanical stability problems, such as electrode delamination, will increase if an amount relatively larger than about 6% of MnO_x is added to regions or layers of the electrode residing at a distance of more than about 20 microns from the electrode/electrolyte interface.

7. It is my belief that one skilled in the art would not understand either JP 5,190,183 or U.S. Pat. No. 5,908,713 to suggest or disclose the performance improvements described above that can be obtained from a fuel cell configured as

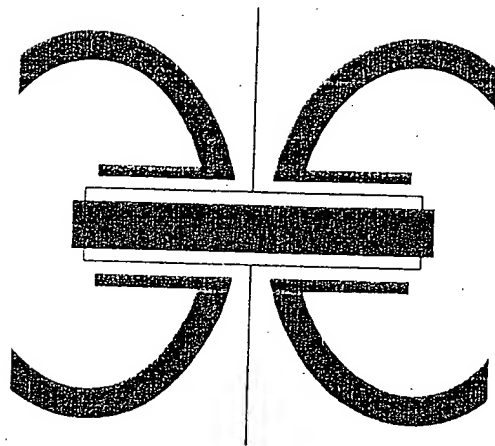
recited in my pending claims. I believe that this is true despite the disclosure of a 1-15 mol% Mn concentration in JP 5,190,183.

8. I declare that all statements made herein of my own knowledge are true and that all statements made upon information and belief are believed to be true.

I further declare that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

19/1-04
Date

Mogens Mogensen
Signature of Mogens Mogensen



Fifth
**EUROPEAN
SOLID OXIDE FUEL CELL
FORUM**

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Development of Thin-Electrolyte Solid Oxide Fuel Cells

Kent Kammer, Peter Halvor Larsen, Ye-Lin Liu, Bruno Kindl
and Mogens Mogensen

Materials Research Department, Risø National Laboratory, Denmark

Abstract

Cells with thin YSZ electrolyte supported by the anode, with LSM cathode and Ni-YSZ anode are fabricated by standard ceramic processing. Anode supports (AS) are produced by tape casting. An active anode layer and an electrolyte are added by slurry spraying. The half-cell is sintered by co-firing. Cathodes are fabricated by slurry spraying. Various pore formers are used in conjunction with different particle size distributions of YSZ to open the structure of the AS allowing for smooth gas diffusion. Different sintering additives have been used either alone or in combination to match the sintering of the AS with the sintering of the electrolyte. The effect of using different types of nickel oxide is also evaluated. The use of MnO_2 as sintering additive resulted in shortening of cell life under extreme conditions due to de-lamination of the cells. Selected cells are tested using humidified hydrogen as fuel. Results with an ASR of about $0.35 \Omega\text{cm}^2$ at 850°C have been obtained. A sketch of the future plans for improving the cell performance is presented.

Introduction

Thin-electrolyte solid oxide fuel cells (SOFC's, thickness of electrolyte less than $20 \mu\text{m}$) are the state of art SOFC's. Thin-electrolyte SOFC's have replaced the thick-electrolyte cells (thickness of electrolyte approximately $200 \mu\text{m}$) allowing for a lowering of the operation temperature from 1000°C to 850°C without a decrease in the performance [1]. Flat plate thin-electrolyte SOFC's are supported on a porous AS normally consisting of a mixture of nickel and yttria stabilized zirconia (YSZ), see figure 1.

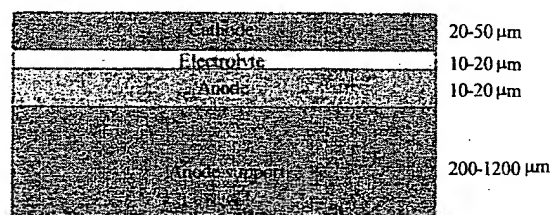


Figure 1. A thin-electrolyte SOFC.

The AS must allow for smooth gas diffusion and a high porosity of the AS is needed. At the same time the AS needs to have a high electronic conductivity as it acts as a current collector. To make the AS porous different tools are at our hands. Either manipulating the microstructure by changing the particle size distribution (PSD) of YSZ or by adding various pore-formers to the tape cast slurry. To assure a high electronic conductivity enough NiO is added to exceed the percolation threshold, that is around 40% (v/v) Ni [2]. An active anode layer and an electrolyte are added to the AS in the green stage.

To control the sintering of the AS and to lower the sintering temperature sintering aids are normally added to the AS. At Risø National Laboratory manganese oxide has been used as a sintering aid giving a strong and highly flexible cell, but other sintering aids can be used as well see i.e. [3].

The cathode is in general consisting of a $(\text{La}_{1-x}\text{Sr}_x)_y\text{MnO}_{3+\delta}$ /YSZ composite. The cathode is normally added in several layers. The cathode is fabricated in such a way that a reaction between LSM and the YSZ electrolyte is avoided. Reaction between LSM and YSZ leads to the formation of non-conducting layers of i.e. $\text{La}_2\text{Zr}_2\text{O}_7$ [4].

To enhance the performance of the cells catalytic active additives can be added to the electrodes, either by impregnation (cathode) or as additives (anode).

Manganese is an example of a catalytic active additive when added to the active anode layer [5].

The performance of the SOFC's is normally evaluated by measuring the area specific resistance (ASR). This can be done by measuring the cell potential as a function of the load. Another important property of the fuel cell is the durability. The durability is evaluated by measuring the ability of the cell to withstand high partial pressure of water under high loads for a long time.

A new generation of SOFC's is under development. The cells are supported on an alternative AS. A ceria-based electrolyte is used instead of the zirconia-based electrolyte. New cathodes materials are under the development. The anode is based on a nickel/ceria composite. The cells aim at an operating temperature of 550°C and redox stability.

The purpose of this paper is to describe the results obtained at Risø National Laboratory when developing thin-electrolyte SOFC's.

Experimental

Fabrication of thin electrolyte solid oxide fuel cells

The AS is produced by standard ceramic processing techniques. In the fabrication of AS different raw materials and sintering aids have been evaluated for optimisation of the shrinkage of the AS and to increase the performance and durability of the solid oxide fuel cells. In some cases the PSD of YSZ has been changed by adding a calcined fraction of YSZ. The resulting slurry is used for tape casting. Tape casting is performed either by hand or on an automated tape caster. After drying the AS is cut into 65x65 or 120x120 cm² pieces. Slurries for spraying of an active anode layer are likewise fabricated by standard ceramic

Slurries for fabrication of the electrolyte layer are made in a similar fashion. All slurries are characterised by measuring the PSD and the viscosity. The active anode layer and the electrolyte are added on top of the green NiO/YSZ tape by slurry spraying, either by a hand-held spray gun or by an automated apparatus. The half-cell is then sintered. A multi-layer layer cathode is added by slurry spraying and sintering.

All powders are characterised by XRD, PSD and BET.

Characterisation of AS and solid oxide fuel cells

The AS is characterised by measuring the linear shrinkage of the cell during sintering or by dilatometry. To further characterise the AS SEM pictures are recorded on sintered pieces of the AS. Leak test of the electrolyte is performed by liquid infiltration. Post mortem analysis of the solid oxide fuel cells is performed by SEM to measure changes in the microstructure and by EDS to observe phase changes.

Testing of solid oxide fuel cells

Cells fabricated as described above are characterised by measuring the electrochemical performance. The cells (with an active electrode area of 16 cm²) are tested in a special set-up designed at Risø. The set-up is described elsewhere [6]. The cells are tested in 97% hydrogen and 3% water vapour and under high humidity conditions (50% hydrogen, 50% water vapour) with a high load (0.5-1 A/cm²). In both cases air is used as an oxidant. Current-voltage curves (IV-curves) are recorded at fixed time intervals to investigate the durability of the cells as a function of the load/humidity. The measurements are performed at different temperatures, but durability studies are done at 850°C.

Results

The linear shrinkage of different AS, by using different sintering aids, NiO, pore formers and PSD is shown in table 1.

Table 1. Linear sintering shrinkage of selected AS. C is calcined YSZ, U is uncalcined YSZ.

| Sintering aid | MnO ₂ | A | B | A | A | A | A |
|---------------|------------------|------|------|------|------|------|------|
| NiO | I | I | I | I | I | I | II |
| Pore former | None | None | None | 1 | 2 | None | None |
| YSZ | C | C | C | C | C | U | U |
| Shrinkage/% | 20.4 | 17.0 | 21.1 | 18.3 | 20.3 | 24.2 | 26.2 |

The linear shrinkage changes from approximately 17% to 21% by changing the sintering aid. Manganese oxide or type B sintering aids are seen to be the most efficient sintering aids. The effect of replacing type I NiO with type II NiO is seen to influence the sintering shrinkage markedly, AS containing type II NiO sinter the most. The effect of using pore-formers results in an overall decrease in the linear shrinkage during sintering, being most severe for type 1 pore former. When the PSD is changed by adding a calcined fraction of YSZ the shrinkage is

likewise lowered. SEM pictures of different sintered NiO/YSZ AS (in oxidised form) are shown in fig. 2a-d. By manipulating the PSD of YSZ and adding pore-formers the structure of the AS is markedly changed. The pore formers clearly leave pores in the structure after sintering. With the addition of a calcined fraction of YSZ pores can likewise be formed in the structure of the AS. The thickness of the sintered AS is in the order of 150-200 μm depending on casting height/composition. The mechanical strength of the sintered AS as evaluated on the background of a simple mechanical test is lower for the foils containing pore formers than for the foils without pore formers.

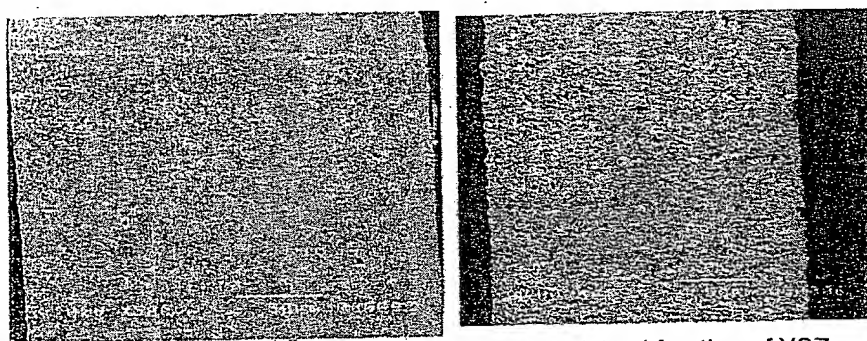


Figure 2a&b. Left typical AS, right AS with a calcined fraction of YSZ.

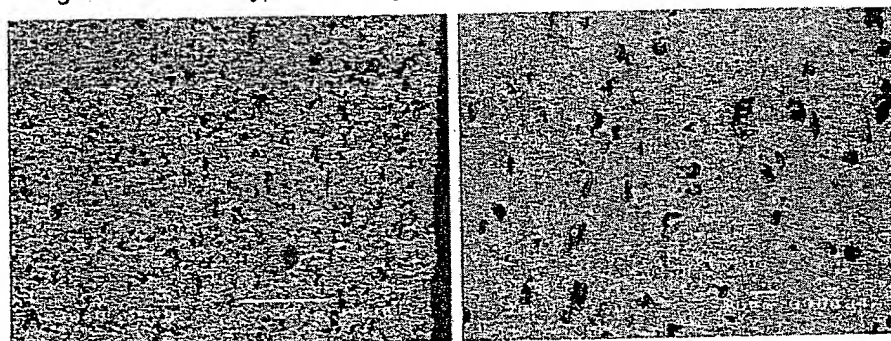


Figure 2c&d. Left AS with type 1 pore former, right AS with type 2 pore former.

The quality of the spraying procedure is revealed in the SEM picture shown in figure 3. The electrolyte thickness is in the order of 10 μm with only a small variation in thickness. In general the electrolyte can be fabricated without pinholes, as long as the thickness of the electrolyte is above 10 μm . The active anode layer in figure 3 has a thickness of around 10 μm . The cathode has a sintered thickness of around 50 μm .

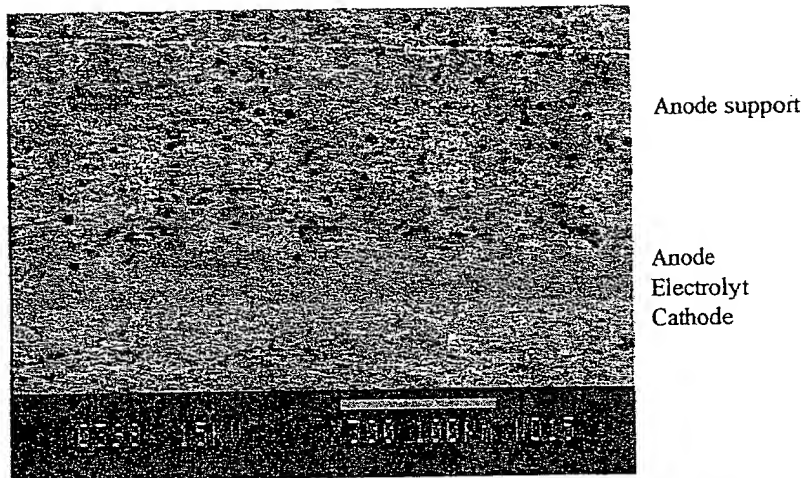


Figure 3. A SEM picture of a thin-electrolyte SOFC.

The result of testing of the cells under high humidity/load conditions can be divided into two groups; the cells containing manganese in the AS and cells with a manganese free AS. The manganese containing cells degraded fast and irreversible typically within hours. A SEM picture of a manganese-containing cell after test can be seen together with the result of an EDX study in figure 4. The white layer is a manganese rich phase.

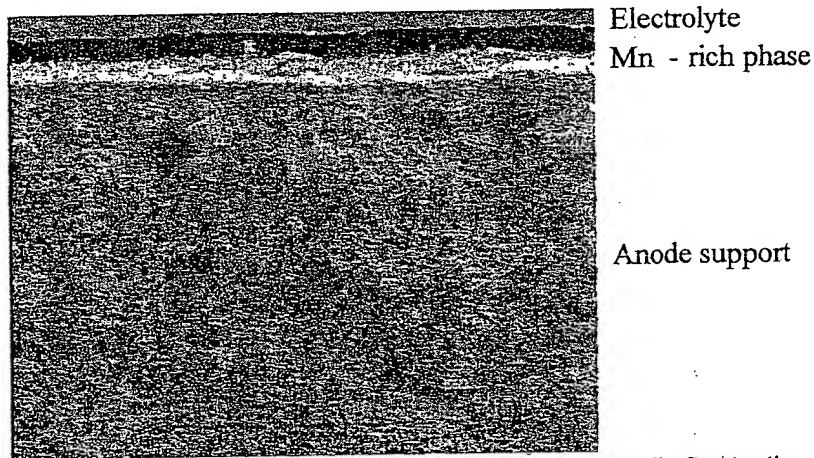


Figure 4. SEM picture of an Mn-containing cell after testing.

It is observed that manganese concentrates at the interface between the electrolyte and the anode. Some of the manganese containing cells delaminated completely resulting in a physical separation of the electrolyte from

the AS during test. An IV curve of a cell (without Mn in the AS) is shown in figure 5.

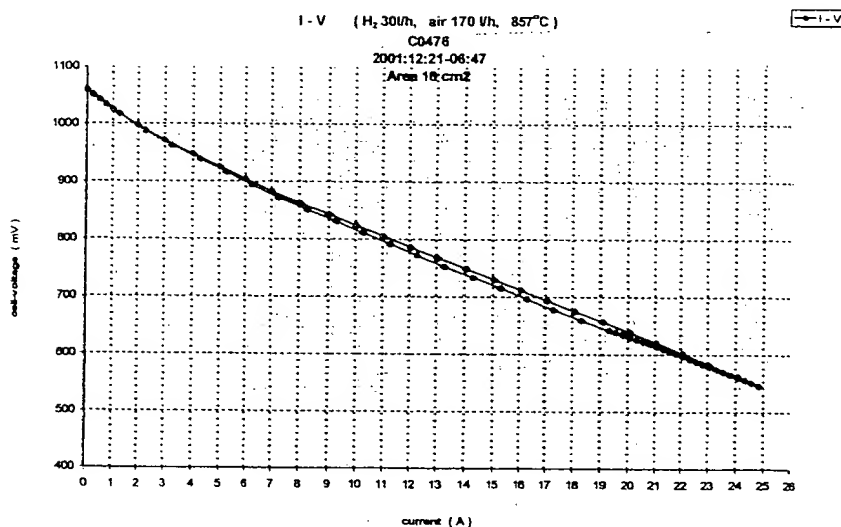


Figure 5. IV-curve recorded at 857°C in humidified hydrogen.

The IV curve shown is recorded in 97% H₂ and 3% H₂O. The initial performance of different cells with manganese in the AS is 0.30 Ωcm² and for cells without manganese in the AS 0.35 Ωcm². The ASR is calculated using OCV as a reference point.

Discussion

The effect of using the type 2 pore former is seen to leave large pores unevenly distributed in the structure. This leads to a lowering of the mechanical strength of the AS. The best effect of pore formers is achieved with the type 1 pore former. The type 1 pore former leaves relatively small and evenly distributed pores in the sintered AS. Changing the PSD of YSZ by adding calcined YSZ has the same effect, but the sintering shrinkage of the AS is markedly lowered. This leads to cracking of cells after sintering. When appropriate sintering aids are used the sintering shrinkage of the AS and the electrolyte can be matched. The PSD, the use of pore formers and the use of type I or II NiO does also influence the sintering shrinkage of the AS and must therefore be taken into account when fabricating cells without cracks.

In practice a gas-tight electrolyte can be fabricated with a thickness of 10 μm by the use of slurry spraying.

The markedly difference in the durability under high humidity conditions of cells with and without manganese in the anode support can be understood from the

SEM picture recorded after the electrochemical test of a cell under high humidity conditions. It is seen that manganese concentrate in the boundary between the anode and the electrolyte. Under high humidity different manganese compounds may form, among them MnH. MnH is volatile and have a vapour pressure of 10^{-9} - 10^{-8} atm when the gas contains 3% water vapour. At higher vapour pressures of water (as at the interface between the anode and the electrolyte) the vapour pressure of MnH decreases [7]. Manganese can therefore be transported in the gas phase from the AS to the anode/electrolyte boundary, where it is deposited. The Mn deposited at the electrolyte/anode boundary may react with Ni and weaken the interface Ni grains in the anode and the electrolyte. This leads to de-lamination of the cells [8]. This problem has been avoided by the use of other sintering aids. The cells without manganese in the AS have an initial performance slightly worse than the cells containing manganese in the AS. As manganese oxide has a positive influence on the performance of the anode this can easily be understood [5].

Plans for Further Work

Further work includes the investigation of other additives than manganese oxide for improving the performance of the anode. The slurries used for the spraying and the apparatus for the spraying of the electrolyte is under optimisation, to be able to obtain gas tight electrolytes with a thickness of around 5 μm . The cathode is improved by optimising the. Cells with a protective layer of ceria between the cathode and the zirconia-based electrolyte are under development. This work aims at a lowering of the operating temperature to 700°C. Work is under way to increase the Redox stability of the cells.

Conclusion

SOFC's with thin-electrolyte has been fabricated by tape casting and slurry spraying. The microstructure of the AS can be tailored using different particle size distributions of zirconia and/or pore formers. Problems with cracks in the electrolyte/AS formed during sintering have been eliminated by matching the sintering shrinkage of the AS with the shrinkage of the electrolyte. The cells perform well with a typical ASR of ca. $0.35 \Omega\text{cm}^2$ at 850°C. Problems with de-lamination of cells under high load/humidity have been eliminated.

Acknowledgements

This work was carried out under the DK-SOFC project supported by the Danish Energy Agency, Elkraft system and Eltra. The colleges at the SOFC-group at Risø are thanked for their support.

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